Kinetic Study of Hindered Amine Light Stabilizer Photografting in Low Density Polyethylene Films under Natural Weathering Conditions

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ABSTRACT: The photografting kinetic of a hindered amine light stabilizer (HALS) was studied in low density polyethylene (LDPE) films under natural weathering conditions. The HALS (PBH-3) was added to the polymer at a concentration of 0.3% (w/w). The photografting kinetic of polymer bound HALS (PBH-3) was determined by direct spectroscopic measurements through the absorption band area of the stabilizer centered at 308 nm in the UV spectra and 1605 cm^{-1} in Fourier transform IR (FTIR) spectra, which correspond to benzylidene malonate ester and benzylidene malonic groups, respectively. In parallel, measurements were carried out on the free PBH-3 content after chloroform extraction of the photostabilizer from the polymer matrix by means of UV and gas chromatography methods. The results showed that in natural weathering the grafting of PBH-3 occurred in the LDPE film after very short exposure times of 127 and 168 h as determined by UV and FTIR, respectively. Moreover, the curves describing both the photografting and the free HALS kinetics exhibited similar profiles. The mechanism of photografting implies a rapid photoreaction between the methylenic double bond of the stabilizer and the macroalkyl radicals of the polymer, resulting in formation of polymer-bonded aminyl derivatives of the stabilizer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1524–1532, 2002; DOI 10.1002/app.10492

Key words: low density polyethylene; hindered amine light stabilizer; photografting kinetic; natural weathering

INTRODUCTION

It is well established that hindered amine light stabilizers (HALSs) are the most efficient photo-stabilizers for polyolefins[1–4] because of their multifunctional activities in the photostabilization mechanisms. These are summarized by Allen and Edge[5] as follows:

1. chain-breaking donor/acceptor redox mechanism through the nitroxyl/substituted-hydroxylamine intermediates,
2. decomposition of hydroperoxides by the amine during processing,
3. inhibition of the photoreaction of α,β-unsaturated carbonyl groups in polyolefins,
4. reduction in the quantum yield of hydroperoxide photolysis,
5. singlet-oxygen quenching (only in polydienes),
6. complexation with hydroperoxides/oxygen,
7. complexation with transition-metal ions, and

8. excited-state quenching by the nitroxyl radical.

Each one of the listed actions may contribute to the overall stabilization process to a certain extent. However, scavenging of alkyl and peroxy radicals is generally considered to be the main mechanism by which HALSs function.[6] As a matter of fact, the literature[7] reported that HALSs are 2–6 times more effective than nickel chelate light stabilizers and 4–10 times more effective than UV absorbers. Most of the works dealing with HALS performance in polyolefins stressed the importance of the persistency of the stabilizers in the polymer matrix during outdoor exposure.[8–12] This is because many antioxidants and stabilizers are known to be readily lost by migration and volatilization when used as additives for polymers.[13] This both reduces their technological performance and creates a potential environmental hazard.[13,14] A simple approach to solve this problem is to increase both the molecular weight of the stabilizers and their solubility.[12] In this respect, Malik et al.[11] suggested that an efficient stabilizer should comply with these three basic requirements: higher solubility or compatibility in the polymer, minimal diffusion, and a high degree of homogeneity of active species in the matrix. However, it was found that the polymeric stabilizers do not satisfy the requirement for homogeneity of distribution of the active piperidine moieties.[11] Subsequently, polymer bound stabilizers were proposed as a possible solution to overcome the problems of physical losses for a longer time. This technique is now being developed commercially in the UV stabilization of polyolefins used for agricultural applications.[13] In fact, new HALSs, such as those designed with low molecular weight (PBH-3), are characterized by their capacity to be grafted to polymer chains by photochemical reactions. These modified stabilizers have one single structure that combines HALSs and UV absorbing units. Therefore, it is expected that better stabilization performance than the polymeric HALS would be obtained.

This article, which is a part of a wider work, deals with the kinetic of photografting of low molecular weight HALS (PBH-3) in low density polyethylene (LDPE) films under natural weathering conditions. In the first part of the study the kinetic of the grafted HALS was determined by direct spectroscopic measurements on film samples through the absorption bands of the stabilizer centered at 1605 cm^{-1} in the Fourier trans-

PBH-3 :   Molecular weight : 528.8 g/mol
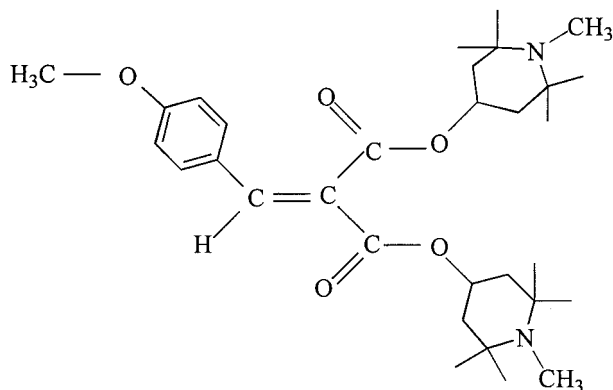
Scheme 1   The chemical structure of the PBH-3 stabilizer.

form IR (FTIR) spectra of the benzylidene malonic group and at 308 nm in the UV spectra attributed to a benzylidene malonate ester. In the second part of the study the concentration of free HALS extracted from LDPE film by chloroform was measured as a function of exposure time using both UV spectroscopy and gas chromatography (GC) techniques. The photografting mechanism of PBH-3 to the polymer matrix was also considered.

EXPERIMENTAL

Materials

The LDPE that was used is manufactured by the Algerian company ENIP and is commercialized under the trade name B24/2. The main physical characteristics of the polymer are a density of 0.923 g/cm^3 and a melt flow index of 0.3 g/10 min according to ASTM D 1238/79. The PBH-3 used is produced by Clariant Company under the trade name Sanduvor PR31. The additive was added to the polymer for stabilization against photooxidation at a concentration of 0.3% (w/w). The chemical structure of the stabilizer and the molecular weight are given in Scheme 1.

Sample Preparation

Films of 80-μ thickness were prepared by the blown extrusion process using a Battenfeld SFB 400 extruder with a length/diameter ratio of 24. The temperature in the extruder varied from 160 to 180°C along the barrel, while in the die it decreased from 180 to 160°C. The films were

stretched in the air after leaving the die at a pulling speed of 5 m/min. They were cooled by air passing through the die into the bubble. Finally, the films were cooled with a large volume of air upward over the surface of the bubble. Wide angle X-ray scattering experiments showed that the as-prepared films did not have any orientation.

Natural Weathering Exposure

The natural weathering of the PBH-3 stabilized LDPE films was carried out according to ASTM D 1435. The samples were in the form of rectangular bands (30 × 20 cm) and were mounted on racks facing southward. The natural exposure was carried out at Béjaia on the East coast of Algeria from December 1999. The exposed samples were removed every 8 h for photografting kinetics analysis.

UV Spectroscopy

The UV spectra were recorded at a resolution of 2 nm with a Shimadzu 2101 PC spectrophotometer equipped with an integrating sphere to avoid the scattered light of the LDPE films. The PBH-3 content in the polymer was determined from the absorption band integration between 263 and 350 nm in the UV spectra. The absorption band area centered at 308 nm in the film and 314 nm in the chloroform after extraction of the stabilizer from the matrix allows the determination of the concentration of the grafted PBH-3 during outdoor exposure.

FTIR Spectroscopy

The IR spectra were recorded using a Shimadzu FTIR spectrophotometer (model 8001 M) with 2 cm^{-1} resolution and 40 scans. All spectra were recorded in the absorbance mode. The typical FTIR spectra of the PBH-3 stabilizer alone and in the LDPE film reveal the presence of two absorption bands centered at 1734 and 1605 cm^{-1} that correspond to ester and benzylidene malonic groups, respectively. The integrated area between 1620 and 1580 cm^{-1} of the absorption band centered at 1605 cm^{-1} was used to determine the amount of chemically bound HALSs during the photografting process. The absorption band of the ester groups at 1734 cm^{-1} was used to measure the concentration of PBH-3 before and after long-term exposure of the samples to natural weathering conditions.

The percentage of retention of the stabilizer was estimated from eq. (1):

$$retention = 100 - loss \qquad (1)$$

where the percentage of loss is calculated from eq. (2):

$$loss = [A_t/A_0] \times 100 \qquad (2)$$

where A_t is the absorption band area of the photostabilizer centered at 308 nm in the UV spectra and 1605 cm^{-1} in the FTIR spectra at a given exposure time and A_0 is the initial absorption band area.

GC Analysis

The determination of the free PBH-3 concentration during the photografting process after removing the stabilizer from the polymer matrix was carried out by GC using a Shimadzu GC-14 B chromatograph. The experimental procedure involved an efficient sample preparation technique using Soxhlet extraction with chloroform for 4 h and a temperature programmed megabore capillary GC with a flame ionization detector. Because of the higher capacity of the megabore column, higher sample quantities can be injected, permitting detection of lower concentrations of additives.[15] The final extracts of 5 μL were injected into the GC. The retention time was recorded, and the area counts were noted. Five runs were carried out to confirm the experimental results.

RESULTS AND DISCUSSION

Kinetic Study of PBH-3 Photografting in LDPE Film under Natural Weathering Conditions by UV and FTIR Methods

Figure 1 shows the UV spectra of unstabilized LDPE film and those stabilized with PBH-3 at a concentration of 0.3% (w/w) and recorded at different exposure times in natural weathering. As expected, the UV spectrum (Fig. 1, spectrum g) relative to the unstabilized sample exhibits no absorption band while the UV spectrum of the stabilized film (Fig. 1, spectrum a) reveals the presence of a large absorption band centered at a maximum wavelength (λ_{max}) of 308 nm before exposition, which is attributed to the benzylidene malonic ester group of the stabilizer. This absorp-
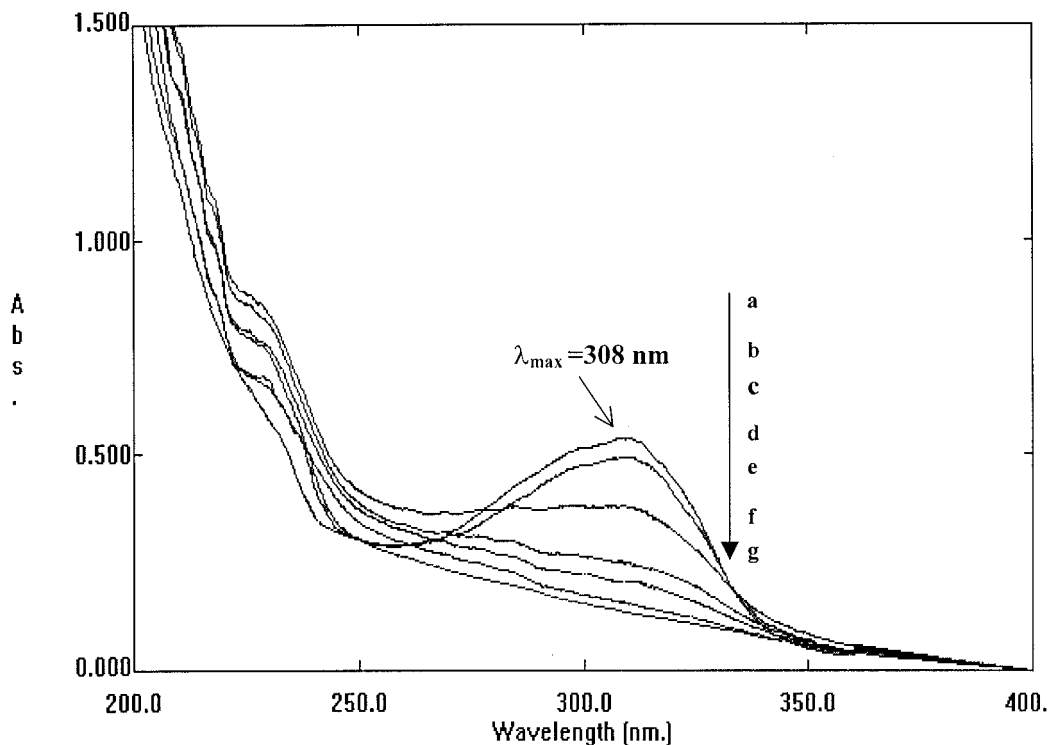
Figure 1 UV spectra of LDPE films stabilized with 0.3% (w/w) Sanduvor PR31 and recorded at different exposure times: the reference sample (spectrum a); samples exposed for 6 (spectrum b), 47 (spectrum c), 72 (spectrum d), 96 (spectrum e), and 127 h (spectrum f); and unexposed LDPE (spectrum g).

tion band is observed to decrease in intensity with time and disappears completely up to 127 h, as illustrated in spectrum f (Fig. 1). Figure 2, on the other hand, shows the FTIR spectra of the LDPE film with 0.3% (w/w) of PBH-3 and recorded in the 1790–1550 cm^{-1} region at different exposure times in comparison with the unstabilized sample. The FTIR spectra of the stabilized samples exhibit two absorption bands: one centered at $\lambda_{max} = 1734$ cm^{-1} that is attributed to the ester group of the stabilizer and one at $\lambda_{max} = 1605$ cm^{-1} that corresponds to the vibration of the aromatic cycle of the benzylidene group. The band centered at 1605 cm^{-1} allows the determination of the amount of grafted PBH-3 during exposure. The FTIR spectra indicate a decrease in the band intensity positioned at 1605 cm^{-1}, which disappears completely up to 168 h. At same time, another absorption band appears that is localized at 1590 cm^{-1}, the intensity of which increases with time. This result may be explained by the rupture of the methylenic double bond, resulting in the shift of the absorption band of the aromatic cycle group to 1590 cm^{-1}. This last result is associated

with the disappearance of the absorption bands observed at 1605 cm^{-1} in FTIR and at 308 nm in the UV spectra and would suggest the occurrence of a rapid photoreaction between the PBH-3 photostabilizer and the LDPE. This reaction causes the stabilizer to be covalently bonded to the polymer matrix through the methylenic double bond. Consequently, the HALS becomes unextractable and highly persistent. This result is extremely beneficial and advantageous for applications involving thin films and fibers in particular.[16]

Figure 3 clearly illustrates the photografting kinetic of PBH-3 in LDPE films under natural weathering conditions. The figure shows the variation of the percentage of retention of the stabilizer in the polymer matrix as a function of time as measured by UV and FTIR. For both spectroscopic methods the curves obtained exhibit a similar kinetic profile characterized by a fast increase in the percentage of retention of the HALS in the polymer matrix during the first days of exposure. In fact, after 24 h of exposure the percentage of retention of PBH-3 as determined by UV is almost 60% and by FTIR is 75%, while the whole grafting
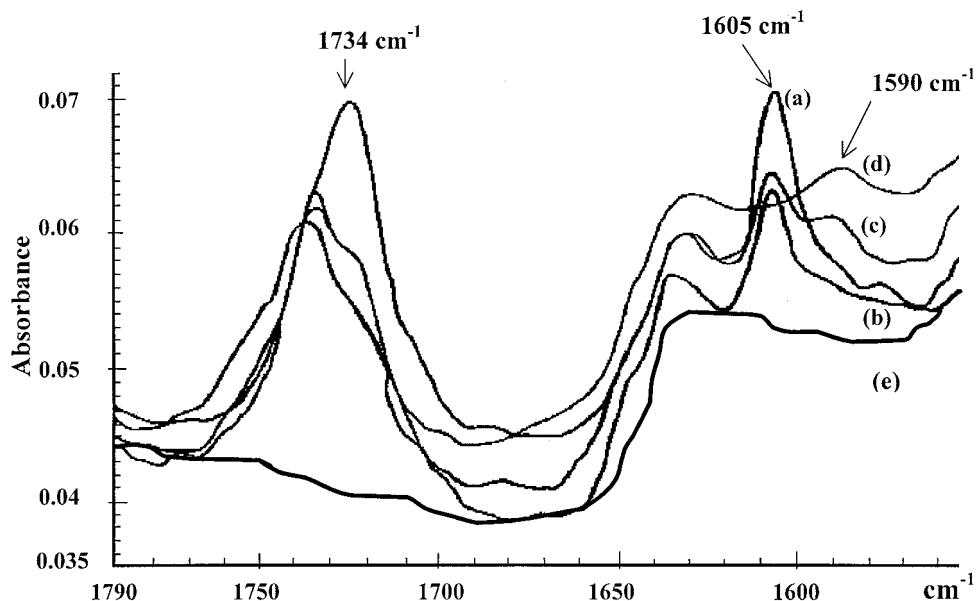
Figure 2 FTIR spectra of LDPE films stabilized with 0.3% (w/w) Sanduvor PR31 and recorded at different exposure times: the reference sample (spectrum a); samples exposed for 6 (spectrum b), 96 (spectrum c), and 168 h (spectrum d); and unexposed LDPE (spectrum e).

of the stabilizer is reached at 127 and 168 h, respectively. Moreover, the figure reveals that the photografting process starts on exposure without showing any induction period.

Kinetic Study of Free PBH-3 after Choloroform Extraction by UV and GC

To confirm the effectiveness of PBH-3 photografting in LDPE films under natural weathering conditions, parallel measurements were carried out
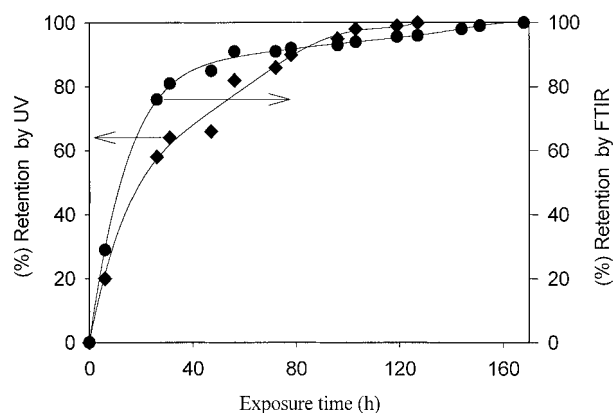

Figure 3 The percentage of retention of PBH-3 stabilizer in LDPE films as a function of the weathering time determined by UV and FTIR.

on the free stabilizer content after the chloroform extraction step. The extracts were analyzed by UV and GC methods and the concentrations of the nongrafted stabilizer determined as a function of time.

Figure 4 shows the UV spectra of PBH-3 in chloroform after extraction of the stabilizer from the polymer matrix and recorded at different exposure times. The figure reveals the presence of a large absorption band positioned at 314 nm in the UV spectrum of the reference sample, which is due to the highly conjugated methylenic double bond. Moreover, a fast decrease in the band intensity at 314 nm is observed with exposure time. In fact, up to 68 h the spectrum (Fig. 4, spectrum e) related to the nongrafted PBH-3 stabilizer shows that the absorption band at 314 nm is almost negligible. This result suggests that the additive is unextractable and subsequently grafted to the polymer matrix. The integrated band areas at λ_{max} = 314 nm measured in the UV spectra give a linear least-squares curve fit against the additive concentration as illustrated in Figure 5. The calibration curve obtained is linear and passes through the origin according to eq. (3):

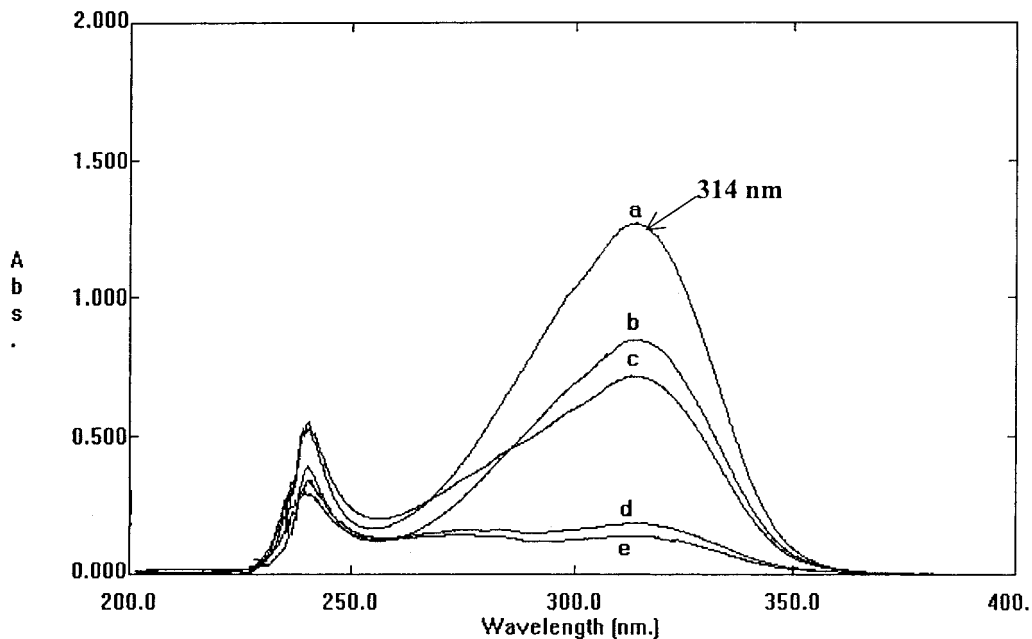$$A_{314} = 2761[\text{PBH-3}] \quad r^2 = 0.999 \qquad (3)$$

Figure 4 UV spectra of the PBH-3 stabilizer after chloroform extraction from the LDPE matrix recorded at different exposure times: the reference sample (spectrum a) and samples exposed for 14 (spectrum b), 17 (spectrum c), 45 (spectrum d), and 68 h (spectrum e).

where A_{314} is the absorbance area of the absorption band centered at 314 nm, [PBH-3] is the concentration of PBH-3 (mg/mL), and r^2 is the coefficient of correlation.

Figure 6 shows the typical gas chromatogram of PBH-3 stabilizer in the chloroform. The figure indicates that the peak of the additive has a retention time of 27.74 min. This result is in good agreement with that reported in the literature[15] for low molecular weight oligomers.

Figure 7 shows the gas chromatograms of PBH-3 after solvent extraction from LDPE films. Chromatogram a is relative to the unexposed sample and chromatogram b is the sample exposed up to 68 h under natural weathering conditions (Fig. 7). In chromatogram a in Figure 7 note the presence of two other peaks besides the typical one of the PBH-3 stabilizer. The retention times for the first and second nonidentified peaks are 15.67 and 21.32 min, respectively. Accord-
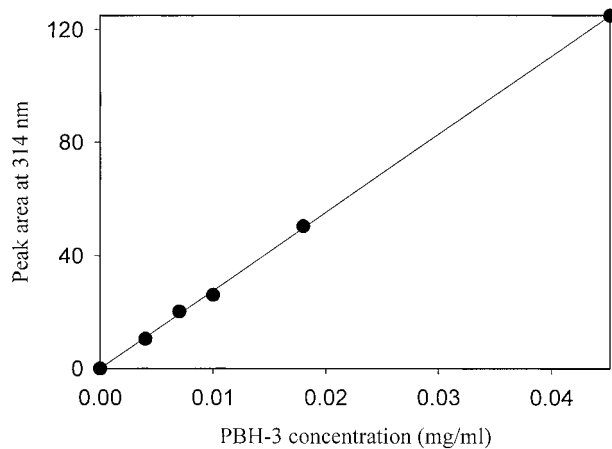

Figure 5 A calibration curve of the PBH-3 stabilizer in chloroform determined by UV spectroscopy.
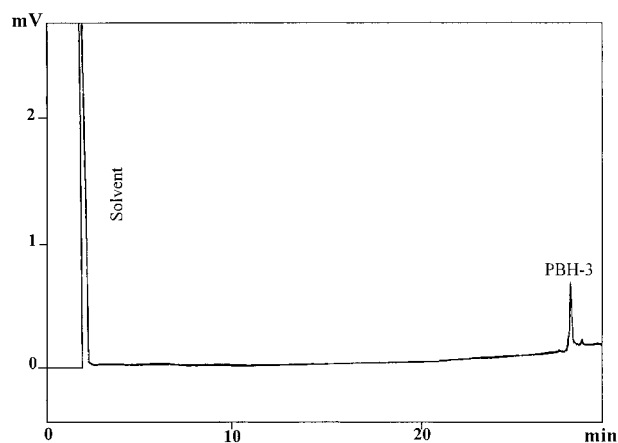

Figure 6 A typical gas chromatogram of the PBH-3 photostabilizer in chloroform.
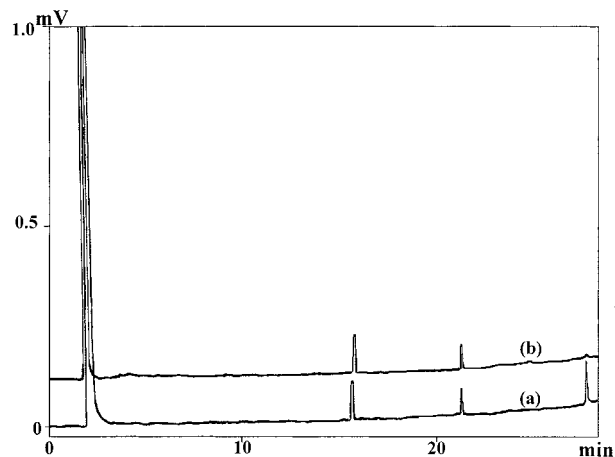
Figure 7 Gas chromatograms of PBH-3 after chloroform extraction from the LDPE matrix: the reference sample (chromatogram a) and the sample exposed up to 68 h (chromatogram b).

ingly, this last result suggests that the commercial LDPE probably contains some other stabilizers like antioxidants added to the material for thermal stabilization. In chromatogram b (Fig. 7), which was recorded at 68 h of exposure, the nonidentified peaks are still present in the extract and seem to not be affected by this short period of exposure. On the contrary, the disappearance of the peak of PBH-3 is clearly observed in chromatogram b (Fig. 7). This last result is comparable to that obtained by UV spectroscopy. This means that the photografting process of PBH-3 occurs rapidly in the first few days of exposure.

Figure 8 describes the photografting kinetics of PBH-3 to LDPE using the decrease of both the UV absorbance and the amount of stabilizer extracted from the matrix determined by GC. The curves
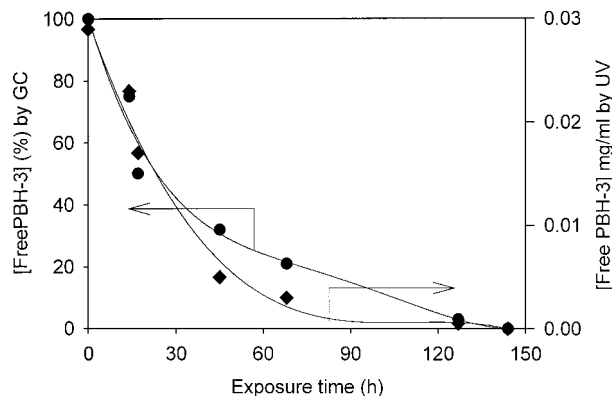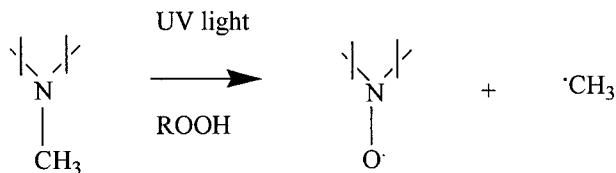

Figure 8 The free PBH-3 concentration versus the exposure time determined by UV and GC.

**Scheme 2** The formation of peridinoxyl radicals.

are almost parallel indicating that after approximately 150 h no free HALSs are present in the exposed samples. This means that the stabilizer is chemically attached to the polymer backbone. These results are consistent with those obtained in the previous section within experimental error.

Photografting Mechanism

Because of the presence of the methylenic double bond in the structure of the PBH-3 photostabilizer, the grafting process occurs by a photochemical reaction. As postulated by Ligner[17] for polypropylene, when PBH-3 is added to the polymer matrix under UV light exposure conditions, the methylenic double bond of PBH-3 reacts with the photoinitiated radicals of the polymer, resulting in the formation of a polymer-bonded stabilizer. The kinetic of grafting will depend on several parameters such as the photostabilizer concentration, the UV radiation dose, the temperature, and so forth. The photografting mechanism probably involves a rapid oxidation of the parent amines (I) to piperidinoxyls (II) with the formation of methyl radicals as shown in Scheme 2. The reaction implying the transformation of I to II is possible under conditions when hydroperoxide is photolyzed.[18–21] Furthermore, this transformation is also supported by the experimental results that are based on electron spin resonance measurements indicating the formation of piperidinoxyl radicals in polyolefins after a few days of outdoor exposure, as reported by many authors.[12,22–24] Acting on the weakly methylenic double bonds, the methyl radicals react preferentially with one carbon radical of the stabilizer while the other one is covalently attached to the polymer backbone, as illustrated in Scheme 3.

CONCLUSIONS

This work demonstrated that the photografting kinetic of a PBH-3 stabilizer in LDPE films under natural weathering conditions is very fast and
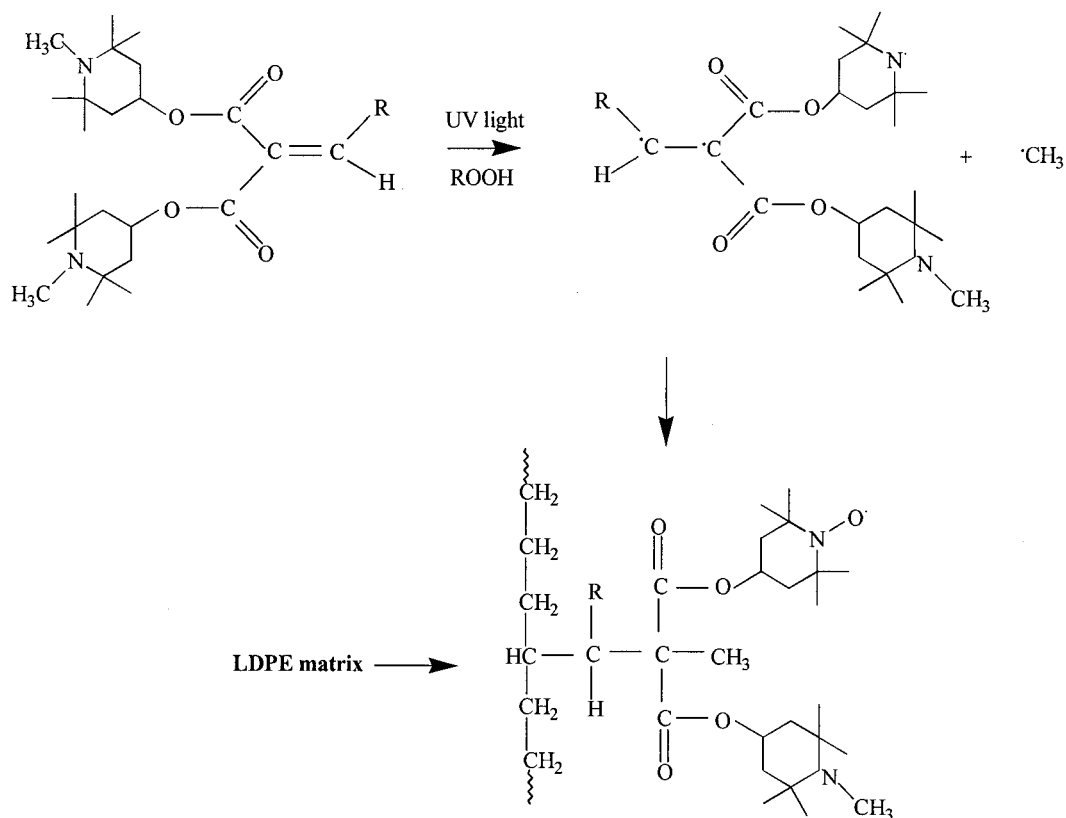
Polymer bound HALS

Scheme 3   The possible mechanism of polymer bound HALS.

occurs in a few days without showing any induction period. In fact, the total grafting of the HALS additive was reached up to 127 and 168 h as determined by UV and FTIR, respectively. This finding is consistent with the data obtained on the free PBH-3 content determined by UV and GC after chloroform extraction of the stabilizer from the matrix. The possible photografting mechanism would imply a rapid photoreaction between the methylenic double bond of the stabilizer and the macroalkyl radicals, resulting in formation of polymer-bonded aminyl derivatives of the stabilizer. This effectively results in grafting PBH-3 to the LDPE backbone, which could possibly avoid the diffusion loss of the additive during aging of the polymer.

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